

NSG-3146

SIZE EFFECTS AND ELECTRON MICROSCOPY
OF THIN METAL FILMS

(NASA-CR-157746) SIZE EFFECTS AND ELECTRON
MICROSCOPY OF THIN METAL FILMS M.S. Thesis
(Texas Univ. at El Paso.) 82 p HC A05/MF
A01

N78-33194

CSCI 11F

Unclas

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SIZE EFFECTS AND ELECTRON MICROSCOPY
OF THIN METAL FILMS

by

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THESIS

Presented to the Faculty of the Graduate School of
The University of Texas at El Paso
in Partial Fulfillment
of the Requirements
for the Degree of
MASTER OF SCIENCE

THE UNIVERSITY OF TEXAS AT EL PASO

August 1978

ACKNOWLEDGEMENTS

I would like to thank Dr. John Brient for his tremendous assistance in understanding thin film phenomena and for his encouragement and invaluable assistance in developing this thesis. I appreciate the help of the other members of my committee: Dr. Bowen, Dr. Dean and especially Dr. Roser for his help in interpretation of the micrographs. I am deeply grateful to Dr. Ellzey for her help and cooperation in the use of the electron microscope and darkroom facilities of the Biology Ultrastructure Laboratory. I would also like to thank Elaine Huizar for her assistance with the electron microscope and darkroom facilities. Mr. Karl Marquardt also must be thanked for his fabrication of parts of the experimental apparatus. To Mr. Rick Longbrake I am grateful for him sharing his experience and urging me into this work. To my co-workers, Don Hammond and Tom Egan, I wish to sincerely thank them for their help and friendship, and especially Jack Elon Graves for his help with the vacuum systems.

Funds for this research were provided in part by a grant from NASA.

August 1, 1978

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INTRODUCTION

A thin metal film is a metal deposited onto a substrate with thickness ranging from several angstroms to several microns. The metal is deposited by means of vacuum evaporation, sputtering, or chemical deposition. Substrates come in varied materials such as glasses, ceramics, single-crystal, and metal substrates. The choice of substrates used depends on the type of study to be conducted since the substrate has a significant effect on the growth and electrical properties of the thin film.

For the research conducted in this thesis, all films are deposited by resistive heated evaporation in an oil diffusion pumped vacuum system (ultimate $\approx 10^{-7}$ torr). Growth of the thin film begins with the condensation of the metal on the substrate. Initially the atoms condense on the substrate surface in the form of small nuclei. These nuclei grow as the evaporation continues and form small islands. These islands grow and eventually, as the evaporation continues, coalesce and form a network of connected islands leaving voids throughout the film. Through continued deposition these channels are filled and form a continuous film. The growth from nuclei to a continuous film is highly dependent on the deposition parameters, evaporation rate as well as substrate material and substrate temperature.

Figure 1 shows the growth stages of a film¹ while Figure 2 shows the dependence of grain size on various deposition and annealing parameters.²

Resistivity measurements are taken on thin films to observe size effects. For size effects to be observed the mean free path must be of the order of the thickness of the film. This ratio is designated by $K_0 = a / l_0$, where a is the thickness and l_0 is the mean free path. The range in which one would like to take measurements is where $.1 \lesssim K_0 \lesssim 10$. This range of K_0 can be approached by taking measurements of one film over various temperatures, since l_0 can be lengthened or shortened by the lowering or raising of the temperature of the film, by measuring films of different thicknesses at one temperature or a combination of different films at different temperatures. For the metals gold³ and silver⁴ the ranges of l_0 are:

¹Leon I. Maissel and Reinhar Glang, Handbook of Thin Film Technology (New York: McGraw Hill Book Company, 1970), pp. 8-33.

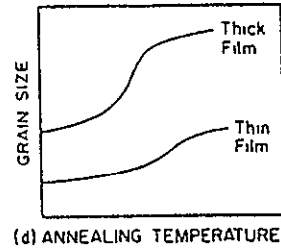
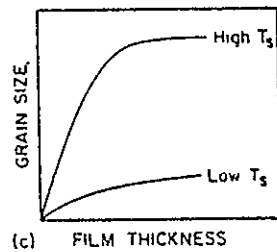
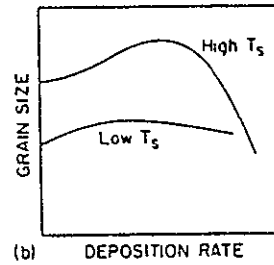
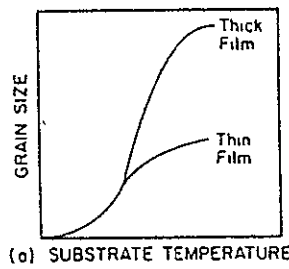
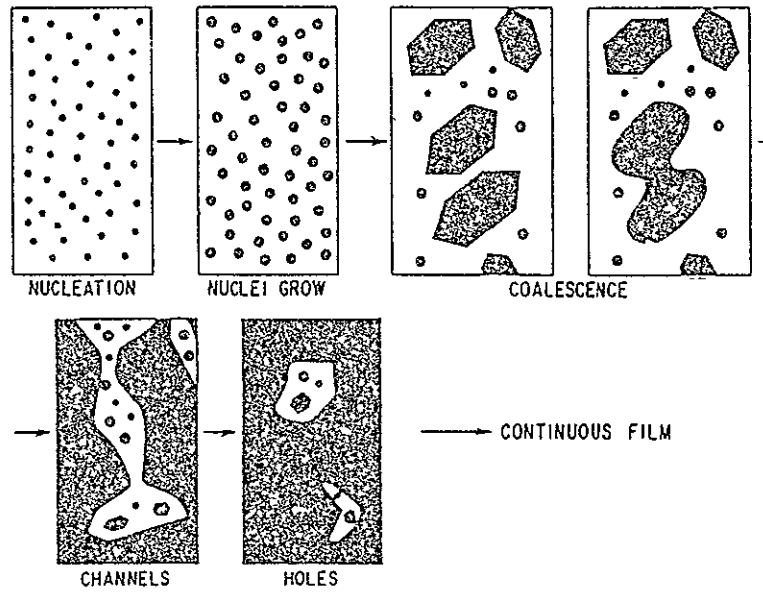
²Kasturi L. Chopra, Thin Film Phenomena (New York: McGraw Hill Book Company, 1969), p. 183.

³K. L. Chopra and L. C. Bobb, "Electrical Resistivity Studies on Polycrystalline and Epitaxially Grown Gold Films," Acta. Metal., 12 (1964), pp. 807-811.

⁴V. P. Nagpal and V. P. Duggal, "Geometrical Size Effect on Polycrystalline Silver Films," Thin Solid Films, 9 (1972), pp. 313-316.

Figure 1. Stages of film growth.

Figure 2. Dependence of grain size on (a) substrate temperature; (b) rate of deposition; (c) film thickness; and (d) annealing temperature.



Gold	Silver
$l_o \approx 400\overset{\circ}{\text{A}}$ at 298K	$l_o \approx 570\overset{\circ}{\text{A}}$ at 300K
$l_o \approx 1400\overset{\circ}{\text{A}}$ at 78K	$l_o \approx 3200\overset{\circ}{\text{A}}$ at 77K

Therefore measurements are taken on a series of films of different thicknesses in a range of temperatures, although the minimum thickness of a film is seriously restricted at high temperatures. In studying thin metal films, those that are consistently analyzable and well studied are epitaxial films. These consist of single crystal or highly oriented films with large grains. Thus when surfaces are smooth no size effects are observed on these epitaxial films. If these films are grown simultaneously with polycrystalline films in the same evaporation then they would have the same amount of impurities. Therefore a difference between the two could arise from grain scattering in the polycrystalline films.

In the analysis of size effects in the epitaxial films the theory of Fuchs-Sondheimer⁵ is used in which no grain boundary scattering is considered. In analyzing the polycrystalline films the theory of Mayadas and Shatzkes (M-S)⁶ is used since it also incorporates the scattering of the grain boundaries. The resistivity of an epitaxial film

⁵E. H. Sondheimer, "The Mean Free Path of Electrons in Metals," Advances in Physics, 1 (January, 1952), pp. 1-42.

⁶A. F. Mayadas and M. Shatzkes, "Electrical and Resistivity Model for Polycrystalline Films," Physical Review B, 1 (February, 1970), pp. 1382-1389.

with a smooth surface will approach that of the bulk material. Thus the measured resistivity of an epitaxial film will give the ρ_0 to be used in the M-S analysis of the polycrystalline films. Knowing the value of ρ_0 , l_0 can also be determined. Often ρ_0 and l_0 will be different from those of the actual bulk values but ρ_0 and l_0 of the epitaxial films should be similar to that of polycrystalline films when they are evaporated simultaneously.

To grow epitaxial and polycrystalline films simultaneously in the same evaporation different substrates and deposition temperatures will be required. An epitaxial film is usually grown on a crystalline substrate such as mica or NaCl at elevated temperatures while the polycrystalline films are grown on non-crystalline substrates at room temperature. The epitaxial films must be held at a temperature such that the evaporated atoms have enough mobility to orient themselves along the substrate surface. Usually this temperature is well above that of the agglomeration point (this is the temperature where the film begins to revert back to the island structure of its earlier growth).

Looking again at Figure 1 one sees that there is a variation of grain size with substrate temperature. Thus it would be an advantage to be able to vary the substrate temperature of the non-crystalline substrate independently of the crystalline substrates in order to form films of different grain size. Modifications have been made in the experimental apparatus to carry out this type of study.

EXPERIMENTAL APPARATUS

In the research conducted for this thesis the experimental apparatus utilized is basically the same as that described in the theses of Longbrake⁷ and Clark.⁸ In the description of the apparatus emphasis will be on changes and modifications.

Instrumentation

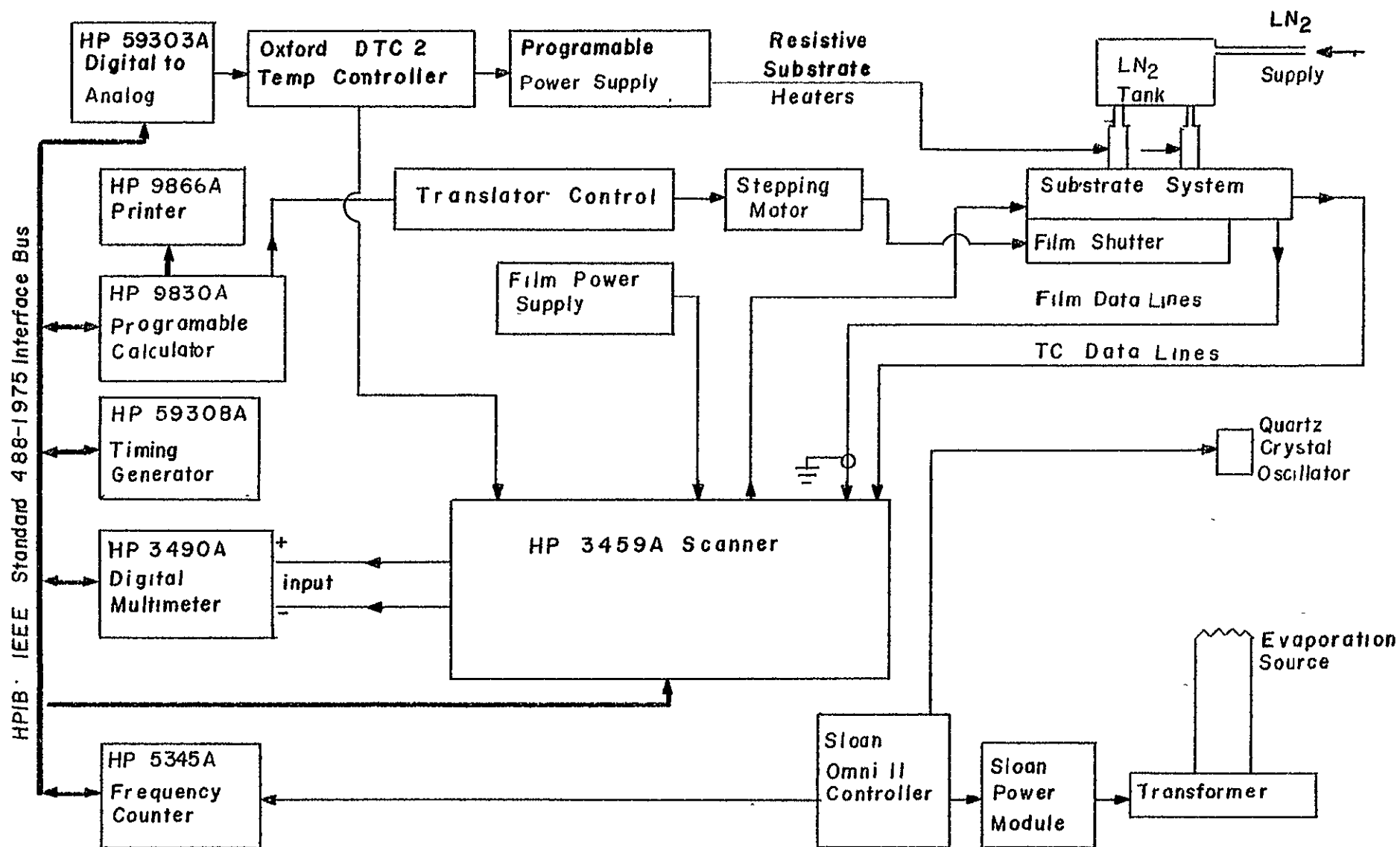
Control of deposition and measurement of films is carried out through the use of a Hewlett-Packard, HP 9830A, calculator interfaced with a number of peripheral devices. Figure 3 is a block diagram of the automated system. The major change in the peripherals is the replacement of the custom built scanner by Clark with the HP 3495A scanner and the addition of a temperature control device, DTC-2 Oxford Digital Temperature Controller.

The DTC-2 monitors a platinum resistance thermometer and the error between the desired temperature and the measured temperature is used to control the amount of power

⁷R. L. Longbrake, "Size Effect and Annealing in Thin Metal Films," Master's thesis submitted May, 1977 to The University of Texas at El Paso, Physics Department.

⁸W. H. Clark, "An Automated Thin Film System For Control of Evaporation and Measurement," Master's thesis submitted August, 1976 to The University of Texas at El Paso, Physics Department.

Figure 3. Block diagram of computer automated system.



to the heaters. The desired temperature is set by inputting a signal of 0-5 volts into the DTC-2 using a digital to analog converter. In addition the DTC-2 outputs a voltage proportional to the temperature measured which is read by the digital volt meter (DVM) and sent to the HP 9830A which allows the temperature of the platinum resistance thermometer to be monitored and recorded.

In the deposition system changes consist of the addition of a thermocouple to the quartz crystal oscillator housing and a source shutter. These attachments were made to enhance the calibration accuracy of the Sloan thickness monitor.*

The automated system is capable of evaporating twelve films of eleven different thicknesses and making resistance measurements from a temperature of 100K to 500K.

Vacuum and Substrate Systems

In this phase of the apparatus the change has been rather dramatic. First the vacuum system used is a 45.72 cm diameter and 80 cm high bell jar with a 15 cm Veeco, Model VE-770, diffusion pump instead of the previous smaller system, 10 cm diffusion pump and a 31 cm diameter 50 cm high bell jar. The distance of the source from the substrate has gone from 31 cm to 54 cm. With this increase there was a smaller variation in film thickness over the substrate area utilized.

* See Appendix.

Initially the substrate system used was the same as that described by Longbrake (see Figure 4). Since we wished to vary the temperature of the two substrates independently, the copper substrate holder was split into two separate pieces. Several evaporations were carried out with this system while still in the smaller vacuum chamber. A temperature difference of only 55K was obtained. At this point the substrate system was redesigned and moved to the larger vacuum chamber. In order to increase the difference in temperature, the copper posts were replaced with stainless steel tubes capped with a copper plug at the ends. Through threaded holes in the copper plugs the tank was attached to the split substrate holder (see Figure 5). As shown in the figure the tubes are asymmetrical in length so as to enhance the temperature difference between each side of the plate. The idea being that when the tank is full of liquid nitrogen (LN_2) both tubes will be at the same temperature. But when the tank is filled to below the protruding tube the side of the substrate attached to it can be heated while the other side continues to be cooled by LN_2 .

This system operated well at a temperature of 400K for the hot side while on the cold side the temperature was 200K. In the metals to be investigated the high temperature side must be above 400K. As the temperature on the hot side was raised above 400K we were unable to maintain independent temperature control and the temperature difference rapidly decreased. Several data runs were taken on this system but

Figure 4. Substrate system.

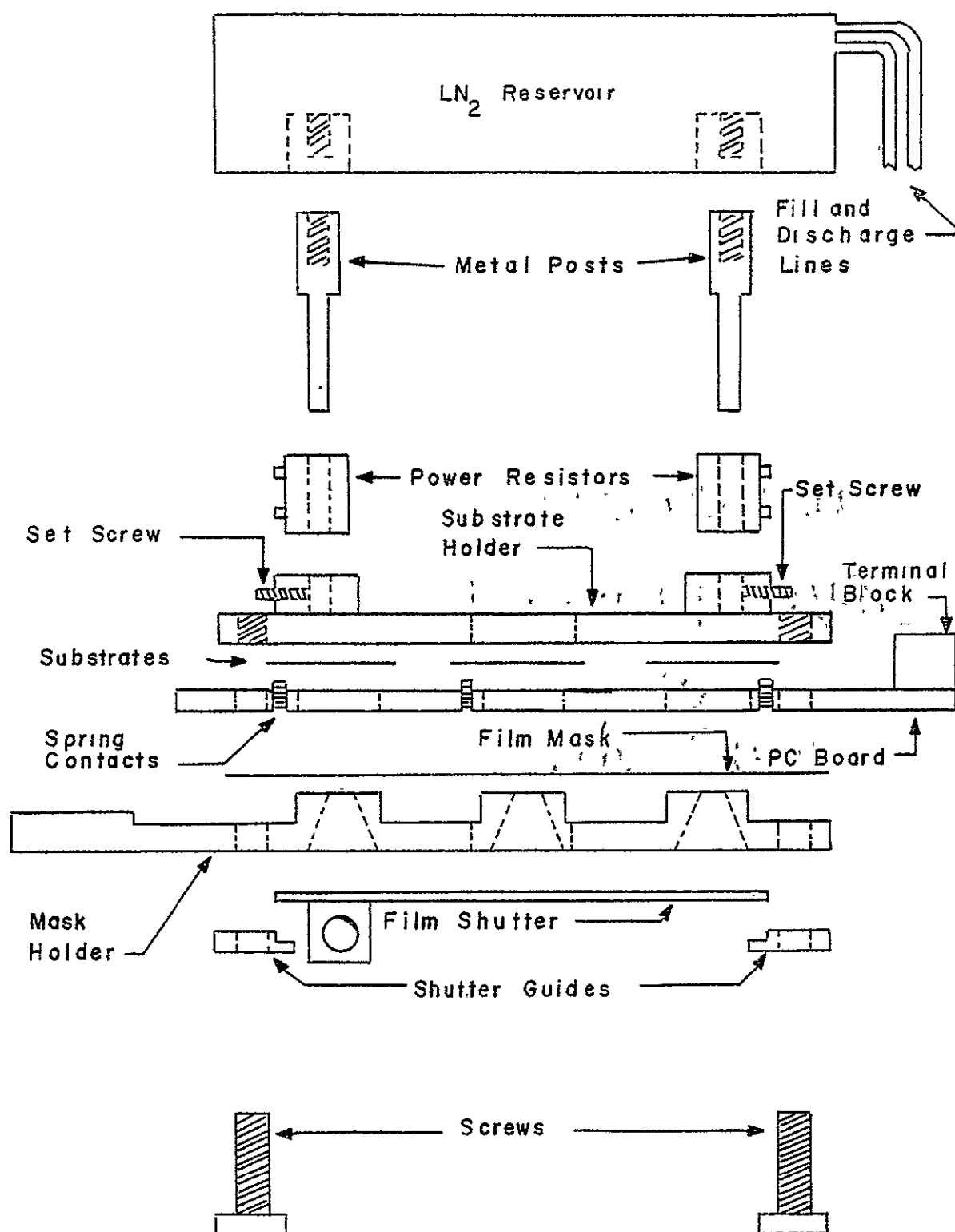
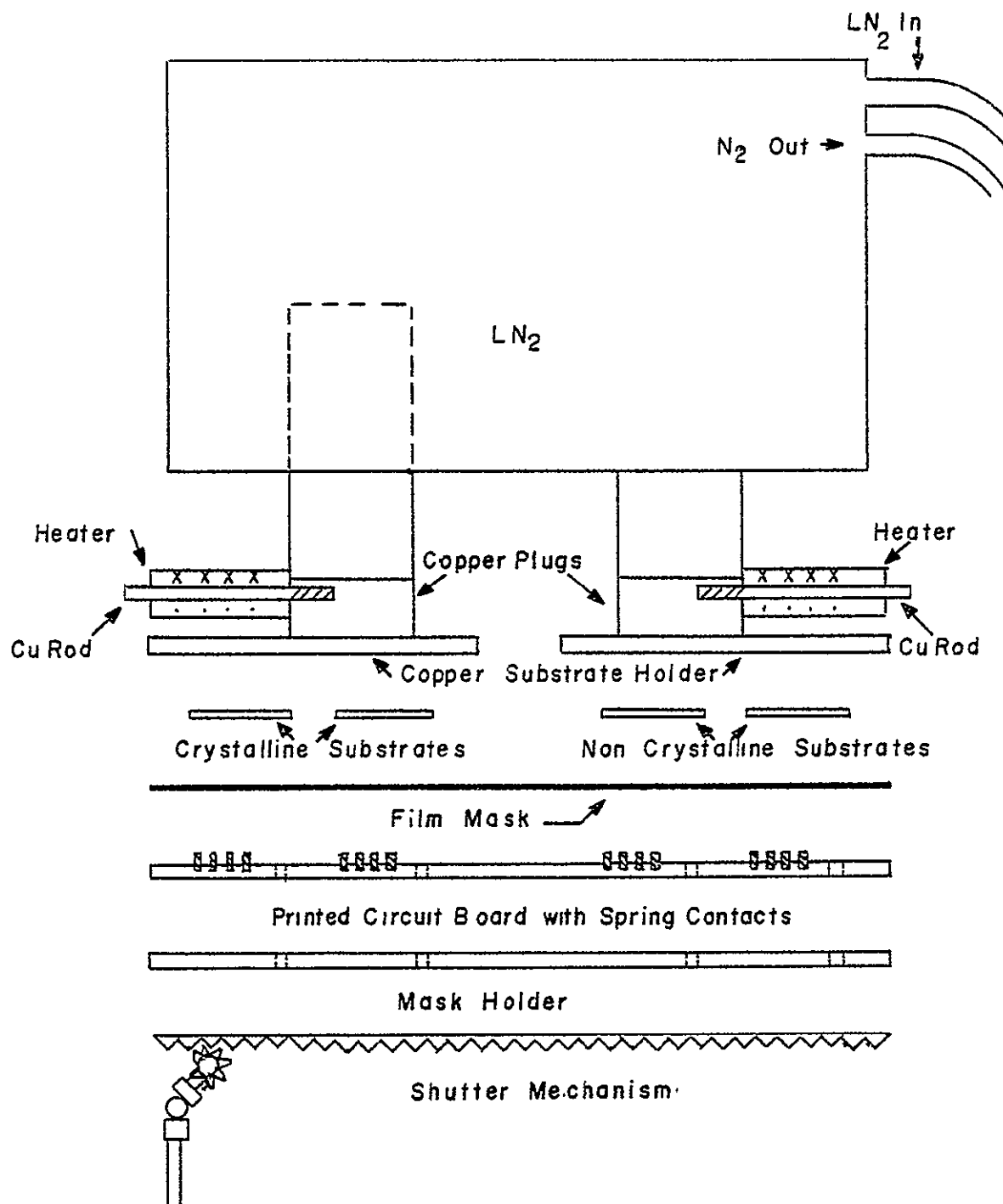


Figure 5. Split substrate system.

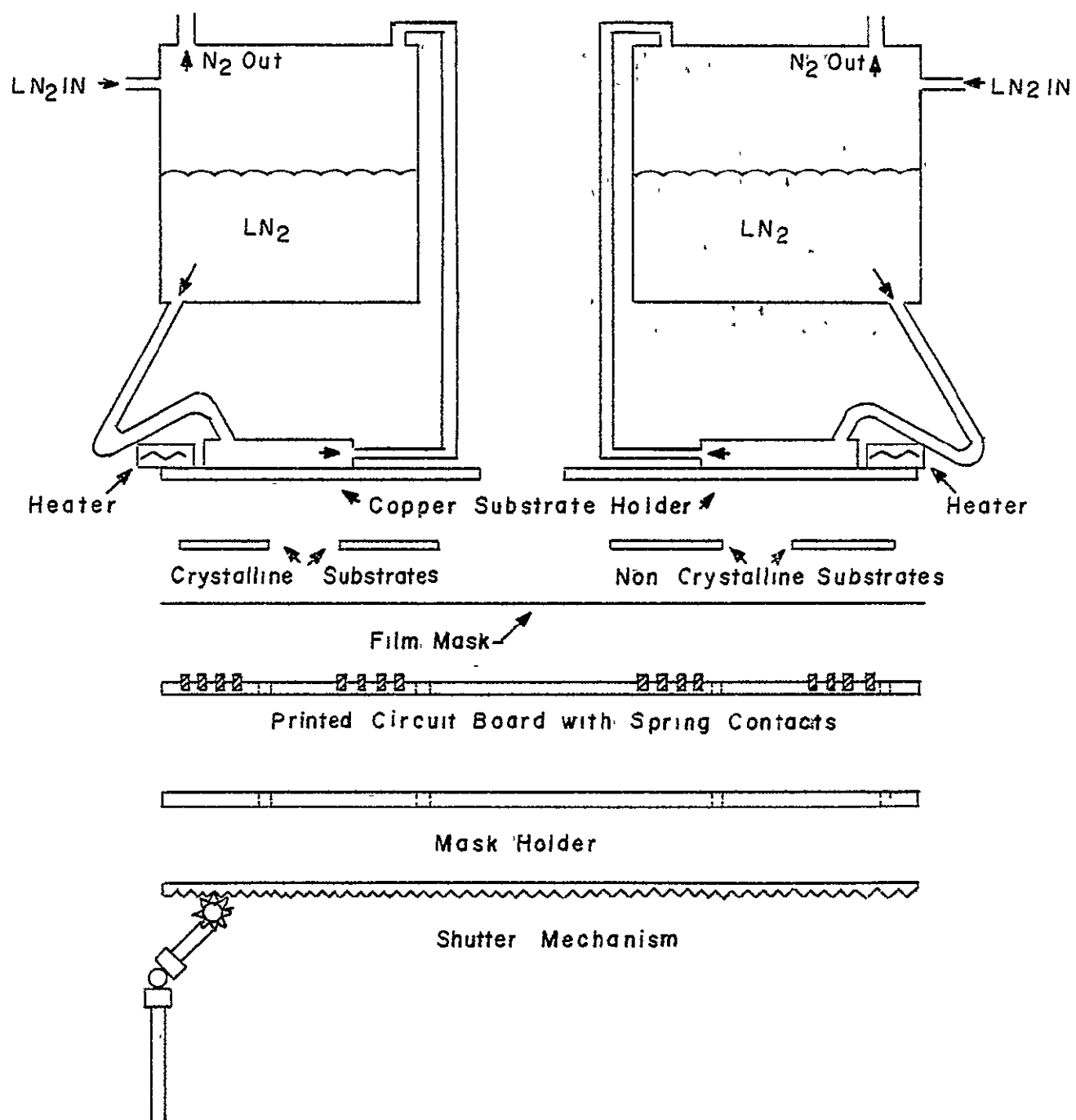


in the deposition mode no attempts at differences in substrate holders were attempted. In addition a continuous substrate holder was used to insure uniform temperature throughout the substrates. The evaporations in this system were all done at 450K. Although this system was not used in the mode for two different substrate temperatures, it was a substantial improvement in extending the range of temperatures measured down to 100K.

In analyzing the past systems the problem was that there was not a complete isolation of one side from the other. A substrate system was designed with a separate heating and cooling system for each part of the split substrate holder. Figure 6 shows this new system. The tank and all the tubing are stainless steel. The tanks are isolated from one another by glass ceramic rods (Corning-Macor) which joins the two separate tanks and give the substrate system a very rigid structure. When this system was being proposed the objective was to obtain temperature differences of at least 200K when the heated side of the substrate holder was raised to at least 450K. Also to enhance the temperature control at low temperatures (100-200K) one must be able to raise the temperature of the substrate holder while liquid nitrogen is in the tanks.

In testing this new substrate system a temperature difference of 375K was achieved while maintaining the heated side at 480K and cooled side at 105K. It is also possible to raise the substrate to 230K while the tank is full of LN_2 .

Figure 6. Split Substrate System.



EXPERIMENTAL PROCEDURE

From start to finish there is approximately three weeks of work involved in one experimental run. It is divided among the preparation of the system, data taking, and analysis (measurement of film dimensions, reduction of resistivity data, taking of TEM pictures, measurements of grain size and determining degree of epitaxy).

System Preparation

In preparing for an experimental run the chamber and all components within must be thoroughly cleaned. Substrates to be used are cut to proper dimensions and cleaned.

Since several metals are used in the research, all traces of these must be removed from the components within the vacuum chamber before another evaporation takes place. Even if the same metal is to be studied the cleaner the system the higher vacuum attainable. Chemical etchants are used in cleaning components with large surface areas in the vacuum chamber while the smaller components are cleaned with Micro Cleaning solution in an ultrasonic cleaner. Once the system is reassembled an alcohol wipe is applied to the large surfaces just before putting it under a vacuum.

A variety of substrates are used in the research carried out. These include pyrex glass (cover slips), Corning 7059 glass, fused quartz, mica and NaCl. For all but

the NaCl the preparations are the same. First they are cut to the proper dimensions using a tungsten carbide scribe on the glass and quartz although the mica is easily cut with scissors. The dimensions needed for one film and its metalizations are 2 x 2 cm. The thicknesses of the substrates are 1.59 mm for the fused quartz, .178 mm for the pyrex glass, .0076 mm for the mica and .533 mm for the Corning 7059 glass. Once cut to the proper dimensions, they are stored submersed in a Micro Cleaning solution until they are to be used. Just before they are to be attached to the substrate holder the container in which they are being stored is placed in the ultrasonic cleaner and the substrates are agitated for five to ten minutes. The mica is an exception to this and is left to be agitated less than one minute. If the mica is left in the ultrasonic cleaner for a longer period of time the agitation will begin to fragment the substrates. Next the substrates are rinsed off with distilled water and blown dry with a hot air gun, being careful not to leave any water spots on the substrates. They are now ready to mount on the substrate holder.

The NaCl was 2 x 2 x 5.02 cm when purchased so that thickness could be varied. The thickness depends on whether the NaCl is to be used alone or in combination with other substrates which would limit the useful range of thickness. Varying the thickness begins with first cleaving a substrate from the NaCl crystal. It is then ground down to close to the desired thickness and then polished to the final

dimension. The grinding process utilized a varying assortment of lapping paper, ranging in grit size from 100 to .3 microns, and a tool on which the NaCl is mounted for grinding and polishing. The polishing is done on a kit designed for the polishing of NaCl windows. Since the thinnest film to be studied is approximately $150\text{\AA}$, the defects on the surface must be much less than $150\text{\AA}$.

The above procedure can be avoided if the NaCl is evaporated onto mica substrates. Koch and Vook⁹ report that a $100\text{\AA}$ film of NaCl evaporated at room temperature on mica will allow smooth epitaxial films of silver to be grown.

For growing epitaxial films, the crystalline substrates must be at high temperatures during deposition. The choice here is whether the non-crystalline substrates are to be at the same temperature as the crystalline substrates or at a different temperature. A continuous copper substrate holder would be used for maintaining all films at the same temperature during deposition. A split substrate holder would be used if the non-crystalline substrates were to be held at another temperature.

Once the substrates are attached to the substrate holder, there is an initial evaporation of metalizations for making electrical contact with films. If a different metal is used for these metalizations than is used for the films

⁹F. A. Koch and R. W. Vook, "Smooth Detachable, (111) Monocrystalline Ag Films," J. Appl. Phys., 42 (1971), pp. 4510-4511.

then the vacuum system is recleaned. The substrate system as shown in Figure 6 is now assembled and ready for film deposition.

Evaporation

The resistive heater evaporation source is a Sylvania Integral Tungsten Alumina Evaporation Crucible. Those with an especially wide opening are used so as to insure a more uniform evaporation.

Before the deposition of any films the substrate system is raised in temperature to bake off and outgas impurities. If there was to be an evaporation at high temperatures or annealing at high temperatures the system should be raised above that point during the outgassing procedure. Usually it is raised beyond the highest temperature to be used in either the deposition or measurement phase. The system is allowed to sit at this high temperature for a period of eight to ten hours while under a vacuum.

At the completion of this final cleaning procedure the substrates now are lowered to the deposition temperature. If a split substrate holder is being used the LN_2 reservoir is filled and the heaters for that side of the substrate holder turned off. The HP 9830A calculator then monitors the temperature of the substrate holder (hot side if the split holder is being used), and will indicate when the deposition controller should be activated. After the deposition controller is switched on the HP 9830A is in full

control until the deposition of films is complete, at which time a manual shutter over the source is engaged. See Clark, et al.,¹⁰ for programing details.

When substrates of different material are used the shutter mechanism covers the films on the non-crystalline and crystalline substrates at the same time. Therefore there will be twelve films of six different thicknesses. The films are numbered from one to twelve and the pairs of films of corresponding thicknesses, from thinnest to thickest, are #1 and #5, #2 and #6, #3 and #7, #4 and #8, #9 and #10, #11 and #12.

¹⁰W. H. Clark, S. J. Brient, R. L. Longbrake and J. Elon Graves, "Automated Apparatus for Evaporation and in situ Measurements of Multiple Thin Films," Rev. Sci. Instrum., 49 (1978), pp. 24-30.

MEASUREMENT

When the film deposition is complete the heaters are turned off and the substrates are allowed to cool down to near room temperature (≈ 90 minutes) before the addition of LN_2 which starts temperature cycling. This is for the case of the continuous substrate holder and the hot side of the split substrate holder. This procedure helps to conserve LN_2 and reduce thermal shock to substrates and films. When the split holder is being used then immediately after completion of film deposition LN_2 is added to cool that part of the substrate that was at the lower temperature. This procedure is used to reduce or prevent any annealing from taking place before data can be taken.

Cooling of the films continues until they reach 100K at which point the measurement routine is initiated. Depending on the film conditions and the type of data required the process of taking data may last up to two or more days running continuously. With the films at 100K the first of four temperature cycles over which data will be taken is begun. As the temperature of the films begins to rise, a measurement sequence is initiated every 10K.

The range over which the films will be measured depends on their agglomeration temperatures. If the films were evaporated at well below their agglomeration temperature then they should at most be raised to just below this

agglomeration temperature. But when they are deposited at temperatures above their agglomeration temperatures then the deposition temperature should be the upper limit of the temperature cycle.

The first temperature cycle is to anneal the films. For a film deposition with substrates at 450K on gold or silver the temperature is cycled over the range from 100K to 450K. The films are then allowed to remain at the highest temperature from one to three hours in order to allow rapid annealing to take place. During the second cycle, the temperature of the films is dropped to 100K and resistivity data is again taken up to 450K at 10K intervals. These two data runs correspond to unannealed and annealed data. For the third cycle the temperature of the films is dropped to 100K but this time a very thin film of from 10 to 50⁰Å is deposited on all the films before the temperature is raised. As the temperature is raised the thin overlayer is annealed. The fourth data cycle obtains measurements on the annealed double layer.

This procedure is basically the same when there are two deposition temperatures, i.e. in the case of the split substrate holder. The only difference would be that the films evaporated at the lower temperatures (those on the non-crystalline substrates) would agglomerate before the films evaporated at the higher temperature. Therefore as the data sequence is carried past the deposition temperature of the films on the cold side (those evaporated at the lower

temperature), the annealing temperature of these films will have to be monitored. When their resistance begins to increase sharply, indicating agglomeration, the temperature cycling will stop at that point and that temperature will be the upper limit for the films during subsequent temperature cycles.

After the last data set has been taken, the films are allowed to reach room temperature before bringing the system to atmosphere. Usually any anomalous behavior of a film during the measurement phase can be understood by looking at the condition of the films and their metalizations after they are removed from the vacuum system. In many cases problems with the films are caused by cracking of the substrates, poor alignment of films with their metalizations, extreme shadowing and noncontinuous films.

Upon completion of the electrical measurement phase thickness measurements (the parameter with the largest experimental error) are taken on the films. Two methods for taking thicknesses are available, a multi-beam interferometer (Sloan Angstrometer) and a profiling device (Sloan Dektak) which uses a stylus. The Dektak measure the film in the region where electrical measurements are actually made. The interferometer cannot measure this thickness without destroying the film for TEM analysis by overcoating. The stylus pressure is set to less than 10 milligrams so that thinner films will not be scratched and to obtain the greatest sensitivity of the Dektak. In taking measurements across the

width of the film, usually three measurements are taken. Each measurement is across the width of the film but in a different location along the length. Thus one can see how uniform the thickness is along the film and obtain an idea of the error in thickness measurements.

In addition to measurements of film thicknesses the Dektak is used to measure substrate smoothness. This is especially critical in the case of NaCl in order to determine when the defects are very much smaller than the films to be measured.

EXPERIMENTAL RESULTS

The four probe resistivity data obtained along with film thicknesses is presented in a normalized form as sheet resistance vs. temperature (sheet resistance = resistivity / film thickness). Table I shows the major deposition parameters of the runs whose data are presented here.

Run Z

Run Z is the only run which utilized the split substrate holder shown in Figure 4. The deposition temperatures 380K and 340K were significantly below the agglomeration temperature 450K.

In this run the thin film added as an overlayer was approximately 10 to 50^oÅ and was evaporated at 220K. Normally following the fourth cycle the run would be terminated but in this run the substrates were then raised to 450K on the mica side and 395K on the glass side of the substrate holder and approximately 150^oÅ was evaporated onto all of the films. Two additional temperature cycles were made up to a temperature of 450K the first to anneal the films evaporated on glass slides and the second to obtain annealed data.

The first of the annealed runs (second temperature cycle) is shown in Figure 7. The data is sheet resistance vs. temperature with the resistance normalized by dividing by sheet resistance at 273K. Pictured separately is the data for the film on mica and those on glass.

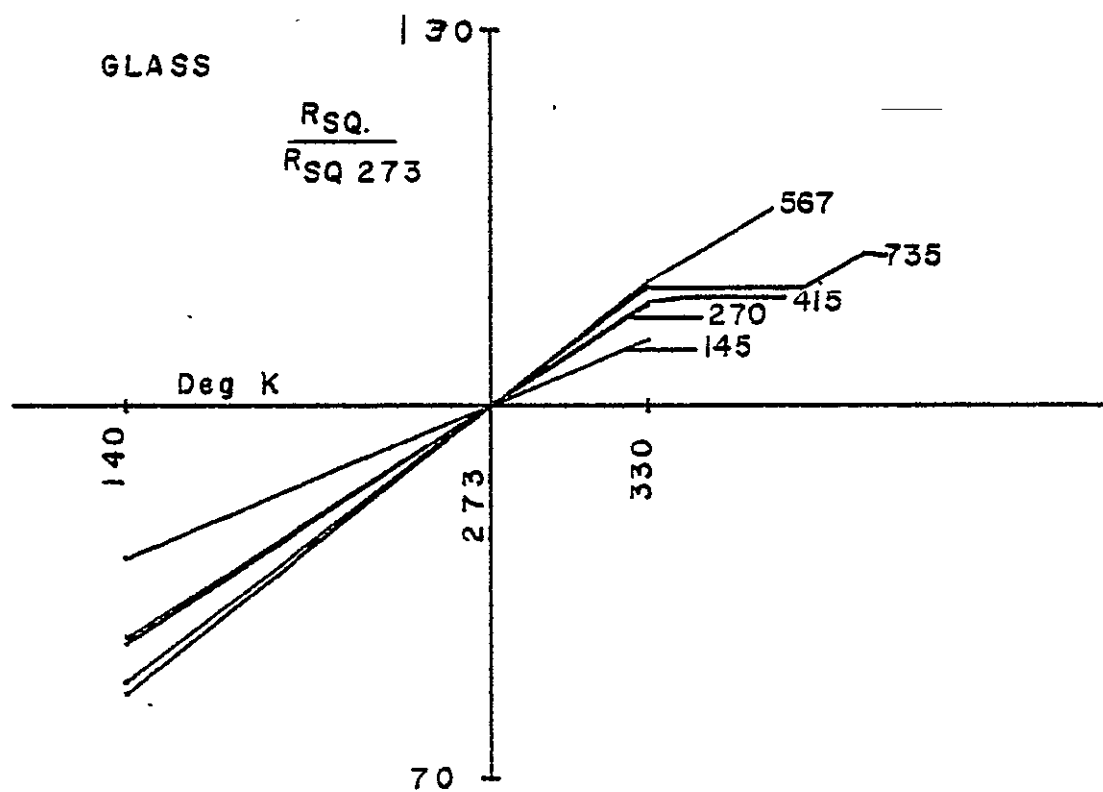
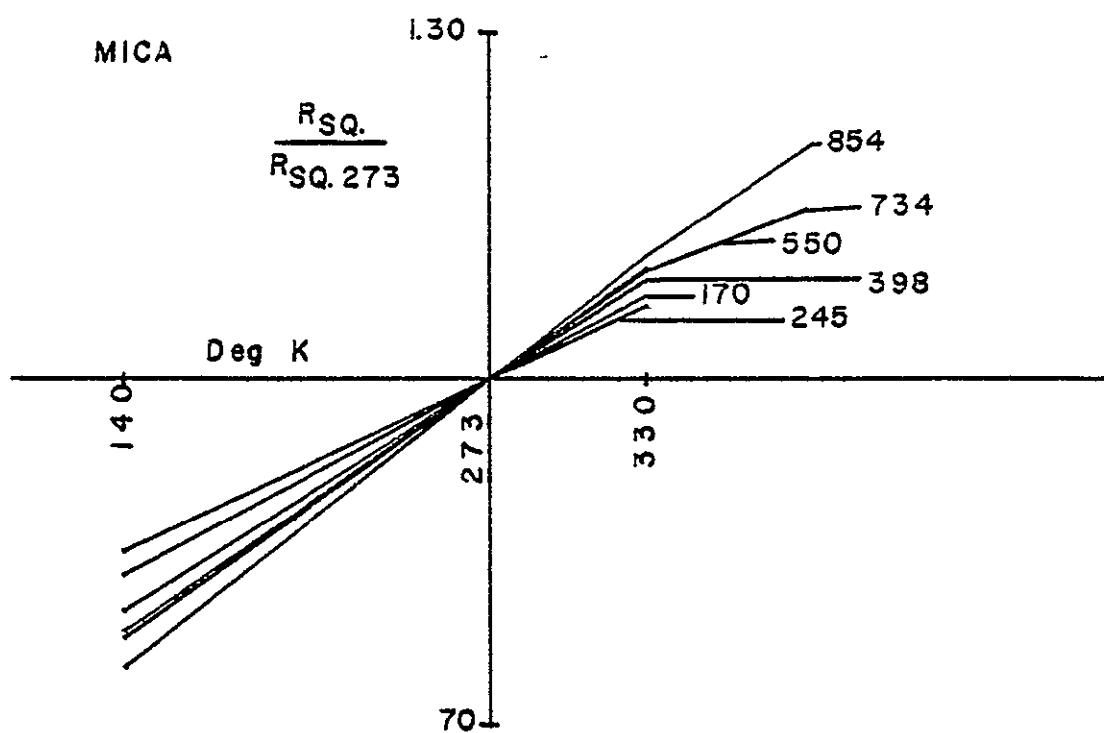
TABLE I

LIST OF RUNS AND THEIR SIGNIFICANT PARAMETERS

Run	Metal	Sub- strates	Deposition Temperature	Deposition Rate	Films Thicknesses (Angstroms)
Z*	Gold	Mica	380K	10 $\text{\AA}/\text{sec}$	170,245,398 550,734,854
		Pyrex Glass	340K		145,270,415, 567,735
F ₁	Gold	Mica	450K	5 $\text{\AA}/\text{sec}$	330,340,650 975
		Pyrex Glass	450K		270,400,650 950
G ₁	Silver	Mica	450K	14 $\text{\AA}/\text{sec}$	316,423,761 714,982
		Pyrex Glass	450K		461,753,910
H ₁	Lead	Mica	450K	28 $\text{\AA}/\text{sec}$	2086,3429 5276,7481
		Pyrex Glass	450K		4269,6510, 9030

*The thickness used are those for the initial evaporation before the additional overlayers.

Figure 7. Normalized sheet resistance (normalized at 273K)
of gold films on mica and glass for Run Z.



Run F₁

This run begins the series of evaporations where both glass and mica are held at 450K during deposition. Data for this run is taken in the range from 100K to 450K over four temperature cycles. Before the beginning of the third cycle a very thin film is deposited onto all films (approximately 10-50⁰A) while the substrates were at 100K. Figure 8 shows the second temperature cycle for mica and glass corresponding to annealed films.

Run G₁

In this run silver is evaporated at 450K well above the agglomeration temperature of all of the films. Figure 9 is a plot of this data. Again this is the data for the second temperature cycle.

Run H₁

Earlier runs were performed on lead using the same range of thicknesses as those of silver and gold but the resistances measured were orders of magnitude greater than those of the gold and silver data. Since the conductivity for lead is about an order of magnitude less than gold or silver the thicknesses of lead were made an order of magnitude greater than those on silver and gold. Looking at Figure 10 for the annealed data on mica and glass indicates very small or no size effect.

Figure 8. Normalized sheet resistance (normalized at 273K) of gold films on mica and glass for Run F₁.

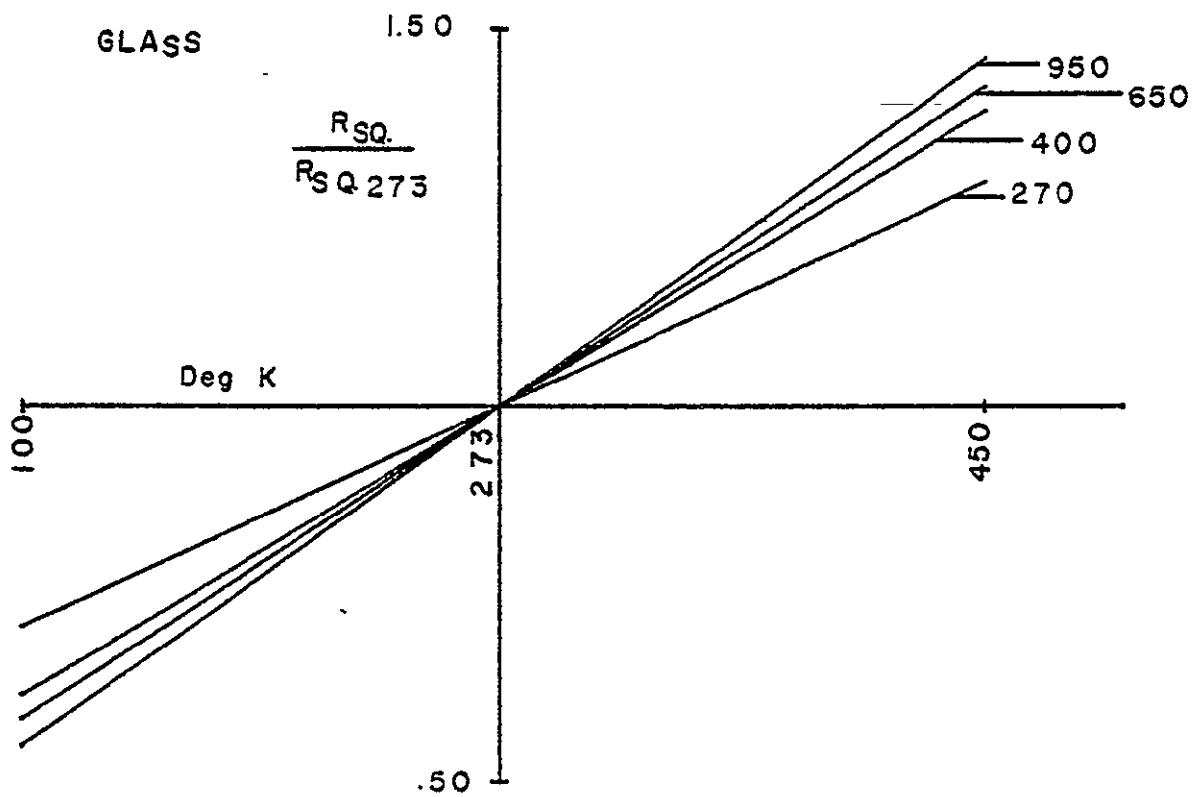
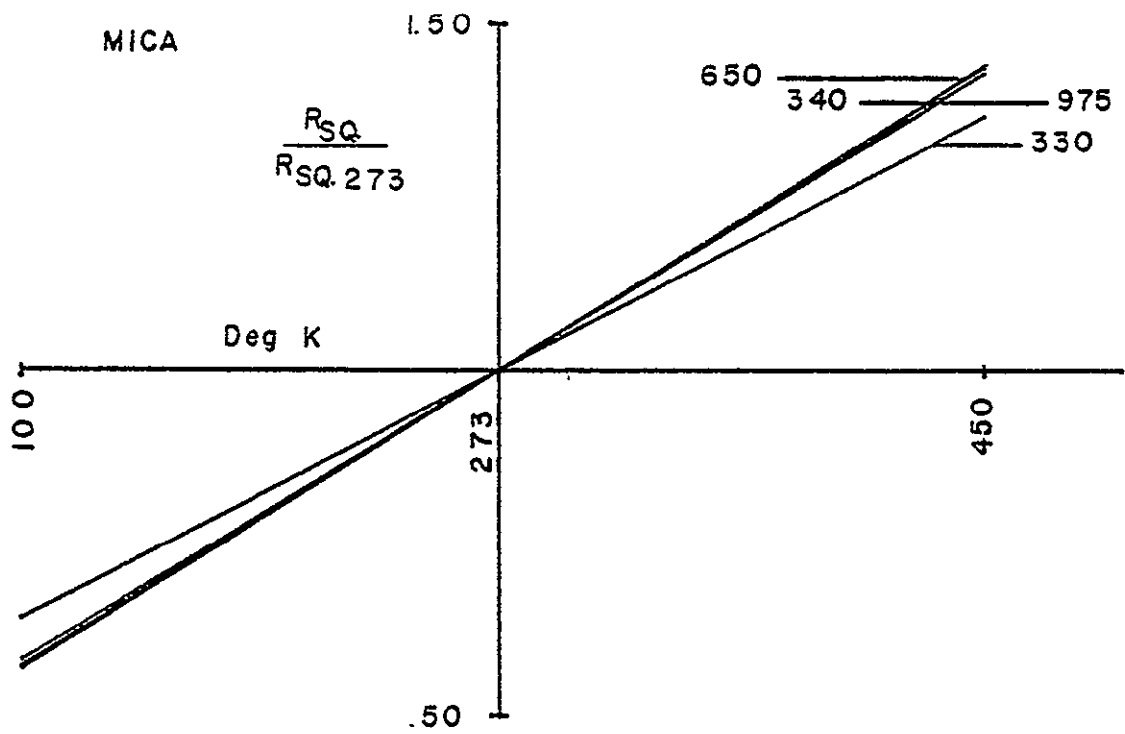


Figure 9. Normalized sheet resistance (normalized at 273K)
of silver films on mica and glass for Run G₁.

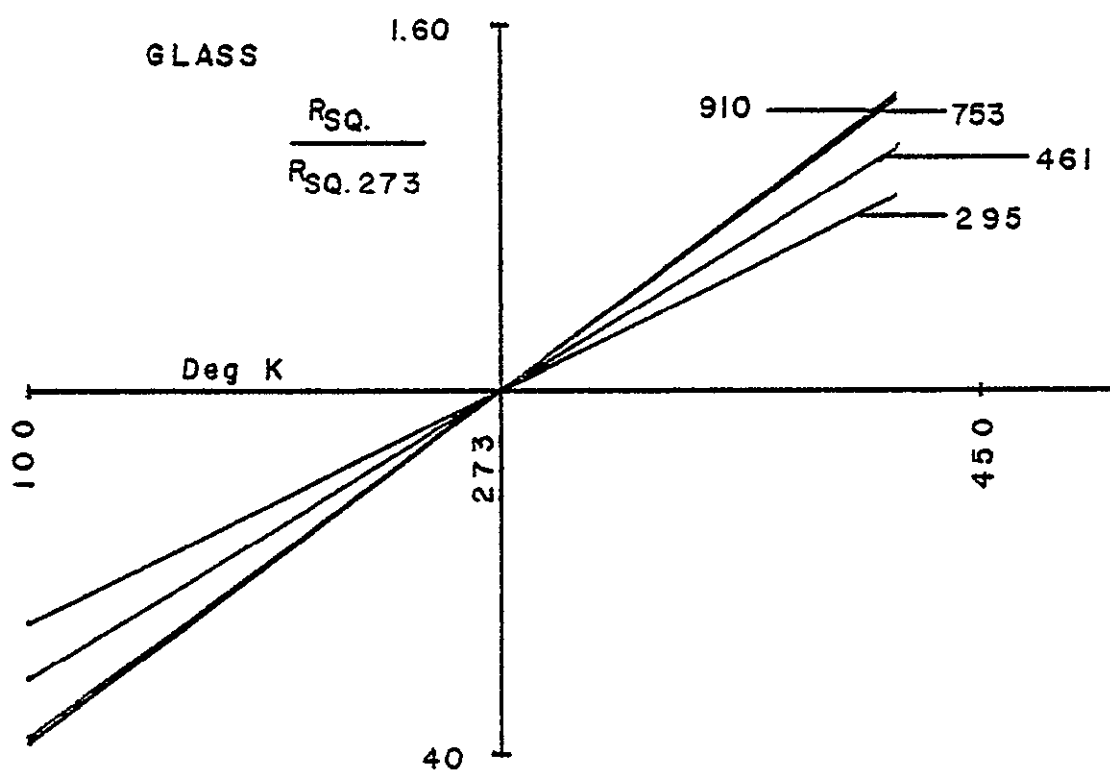
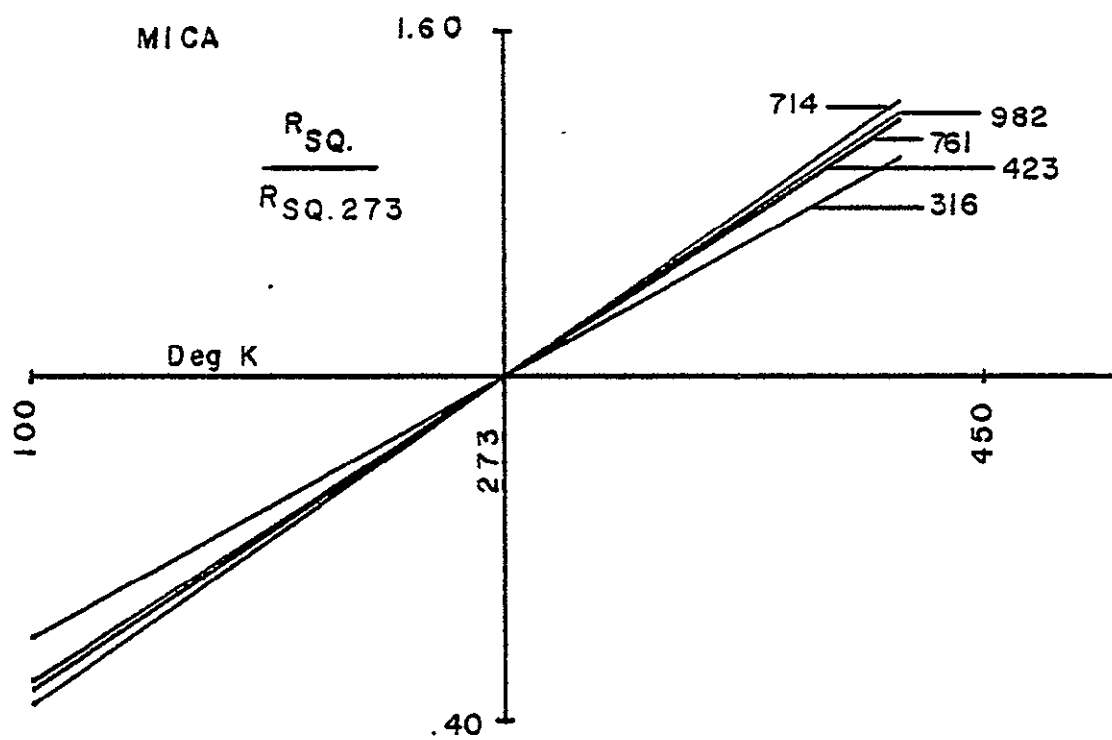


Figure 10. Normalized sheet resistance (normalized at 273K) of lead films on mica and glass for Run H₁.

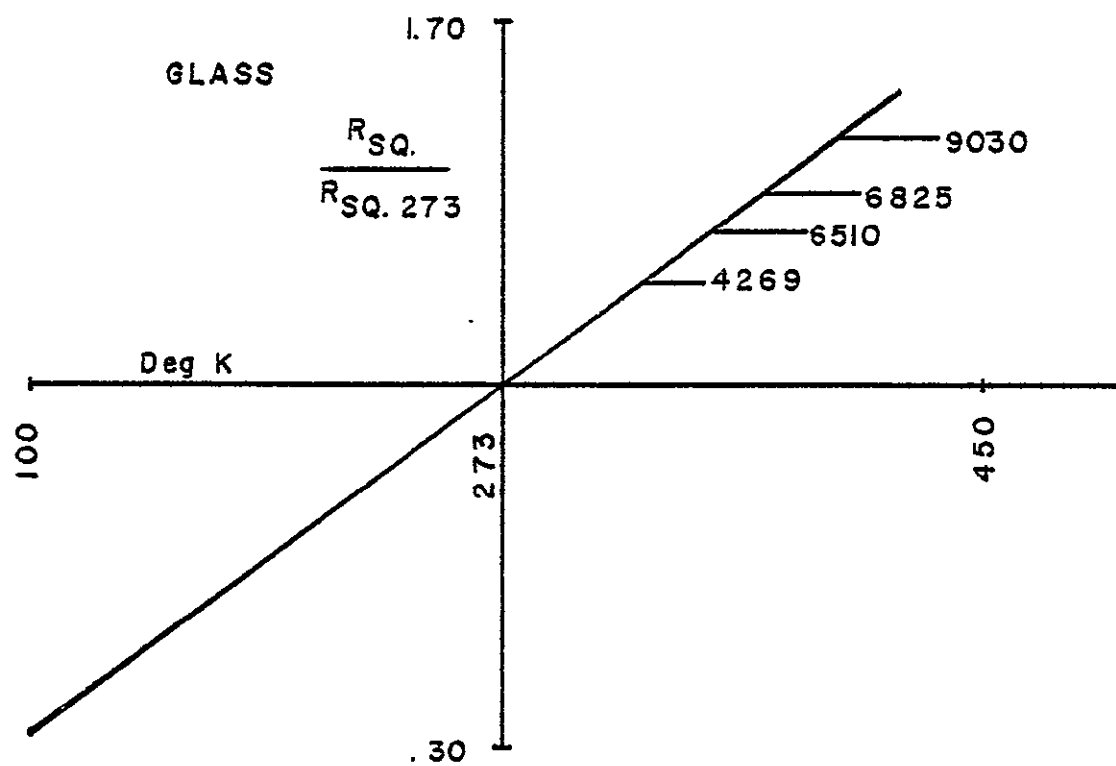
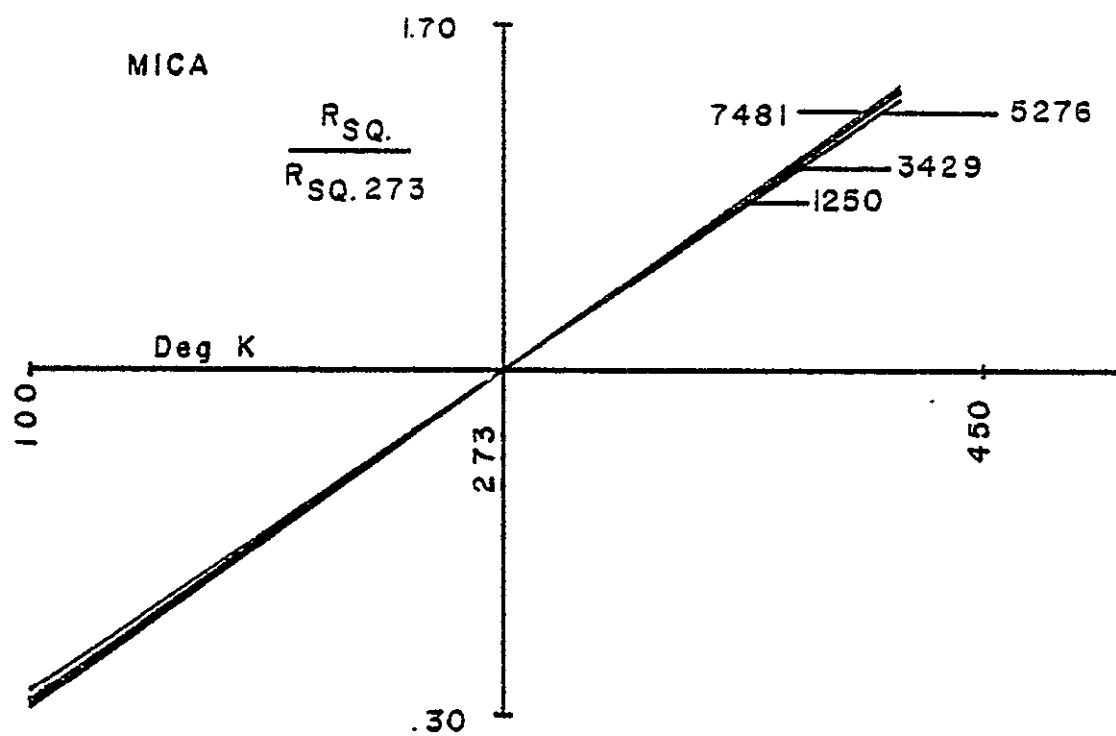


Table II is a list of the slopes and intercepts for the normalized data plotted.

TABLE II

SLOPES AND INTERCEPTS OF NORMALIZED DATA

Run	Thickness (Angstroms)	Slope ($\times 10^{-3}$)	Intercept
Z Mica	170	1.27	.652
	245	1.12	.695
	398	1.51	.589
	550	1.64	.551
	734	1.69	.539
	854	1.88	.487
Z Glass	145	.921	.749
	270	1.41	.616
	415	1.44	.606
	567	1.75	.523
	735	1.67	.544
F ₁ Mica	330	2.07	.43
	340	2.47	.33
	480	2.26	.94
	650	2.49	.32
	975	2.42	.34
F ₁ Glass	270	1.68	.54
	400	2.22	.39
	650	2.40	.34
	950	2.61	.29
G ₁ Mica	316	2.62	.29
	423	3.06	.16
	761	3.06	.17
	714	3.30	.10
	982	3.15	.14
G ₁ Glass	295	2.20	.40
	461	2.74	.25
	753	3.29	.10
	910	3.36	.08
H ₁ Mica	1250	3.88	-.058
	2086	3.89	-.062
	3429	3.97	-.083
	5276	3.77	-.028
	7481	3.92	-.069
H ₁ Glass	4269	3.88	-.060
	6510	3.92	-.069
	9030	3.88	-.060
	6825	3.87	-.057

ELECTRON MICROSCOPY STUDY

For the electron microscopy study a series of transmission electron micrographs and diffractographs were taken of selected films from runs Z, F₁ (both gold) and G₁ (silver). A Zeiss EM10 electron microscope operated at 100kv was used. A 50 micron intermediate aperture was used for the selected area diffraction on all but one of the films (Figure 12e). The aperture size corresponds to a 1 micron specimen area. The micrographs allow the average grain size of a particular film to be determined. The lack of continuity, i.e., the amount of voids any particular film may have can also be determined from the micrographs. The degree of orientation, whether preferred or random, was achieved through the use of diffractographs. To some extent these diffractographs can be used to investigate the average grain size of a film. This is because the small aperture allows the diffraction spots to be resolved individually, such that the more dense the amount of diffraction spots the more grains in the area investigated.¹¹

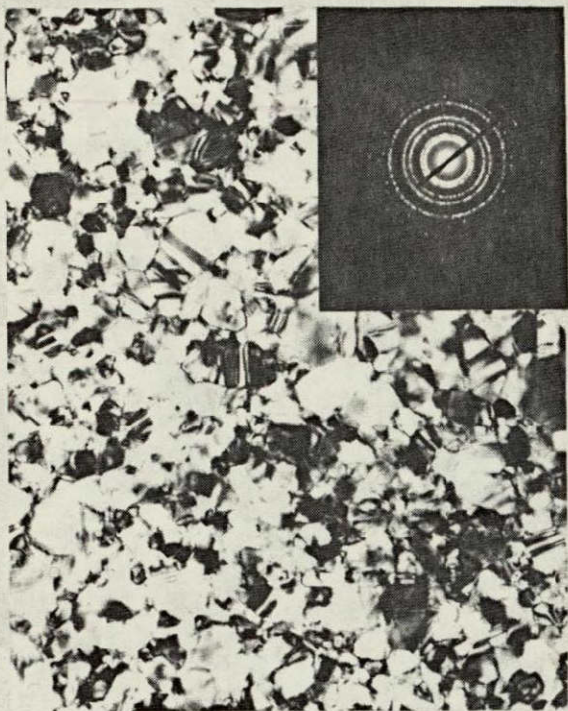
Run Z

The films from run Z are shown in Figure 11.

¹¹Gareth Thomas, Transmission Electron Microscopy of Metals (New York: John Wiley and Sons, Inc., 1962), pp. 28-29.

Figure 11. Run Z (a) film #1 $295\overset{\circ}{\text{\AA}}$, and (b) #4 $773\overset{\circ}{\text{\AA}}$ were deposited on mica at 380K, (c) film #5 $270\overset{\circ}{\text{\AA}}$, and (d) #8 $790\overset{\circ}{\text{\AA}}$ were deposited on glass at 340K.

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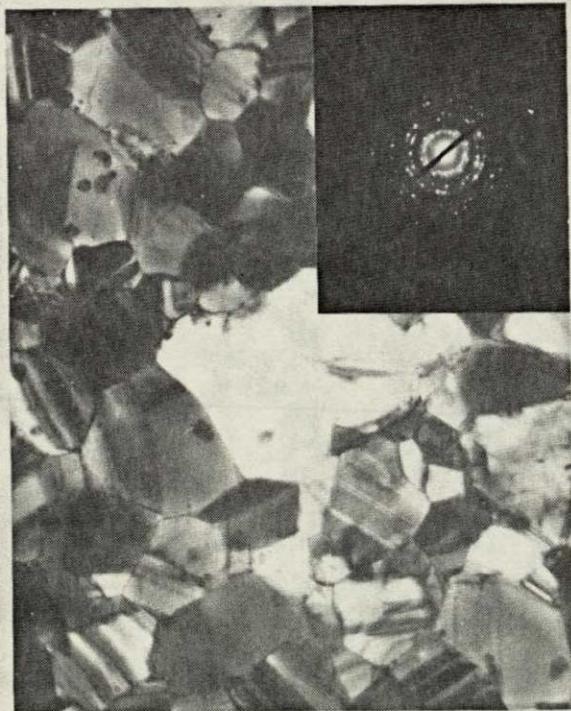


a



c

1700 Å



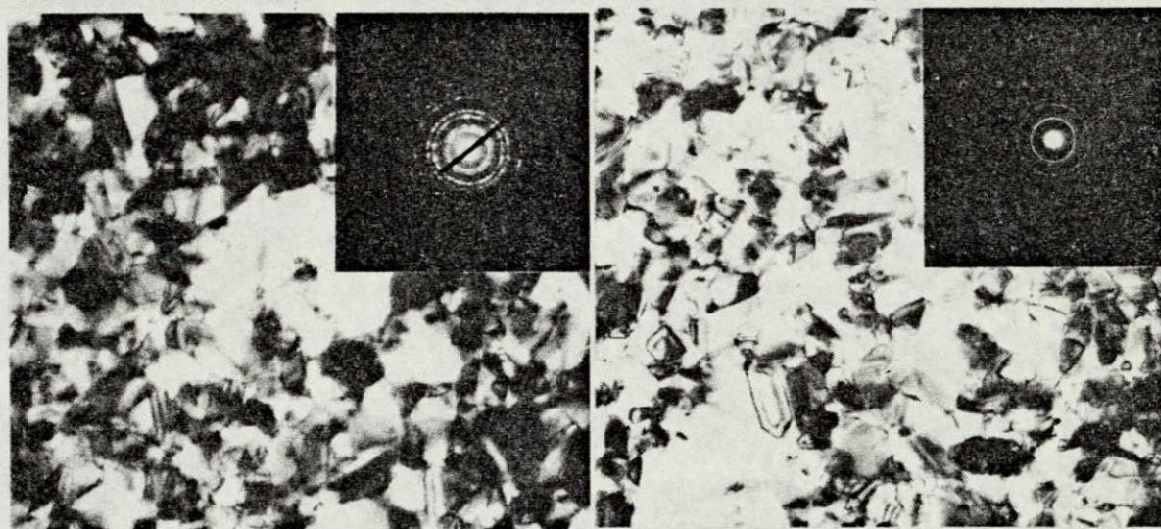
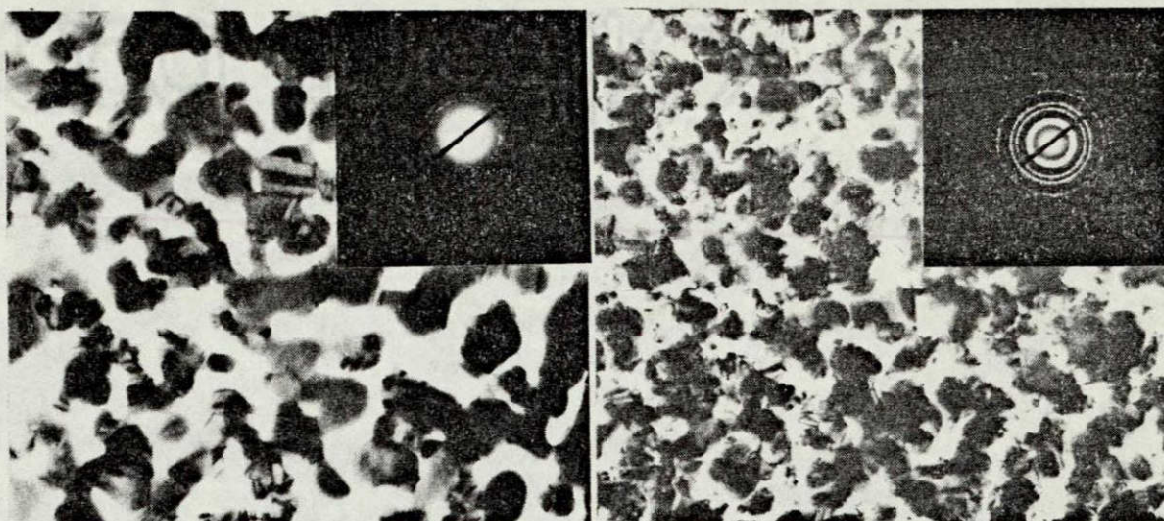
b



d

Figure 12. Run F_1 (a) film #1 $< 200\text{\AA}$, (b) #4 $480\text{\AA}$, and (c) #12 $975\text{\AA}$ were deposited on mica at 450K, (d) film #5 $< 200\text{\AA}$, (e) #7 $400\text{\AA}$, and (f) #10 $650\text{\AA}$ were deposited on glass at 450K.

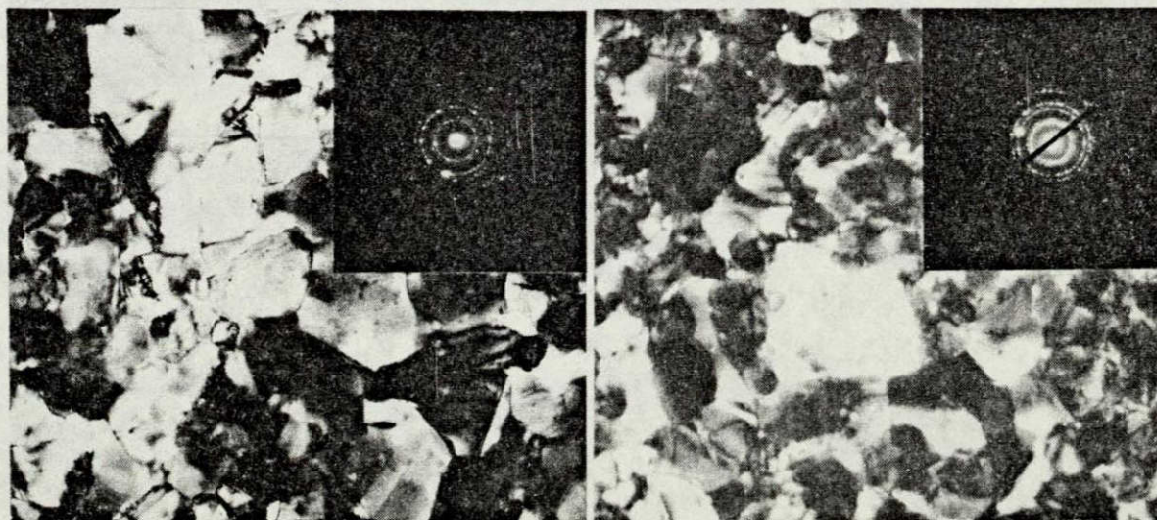
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b

1700 Å

e



c

f

Figure 13. Run G_1 (a) film #3 $423\overset{\circ}{\text{\AA}}$, and (b) #4 $761\overset{\circ}{\text{\AA}}$ were deposited on mica at 450K; (c) film #6 $295\overset{\circ}{\text{\AA}}$ and (d) #8 $753\overset{\circ}{\text{\AA}}$ were deposited on glass at 450K.

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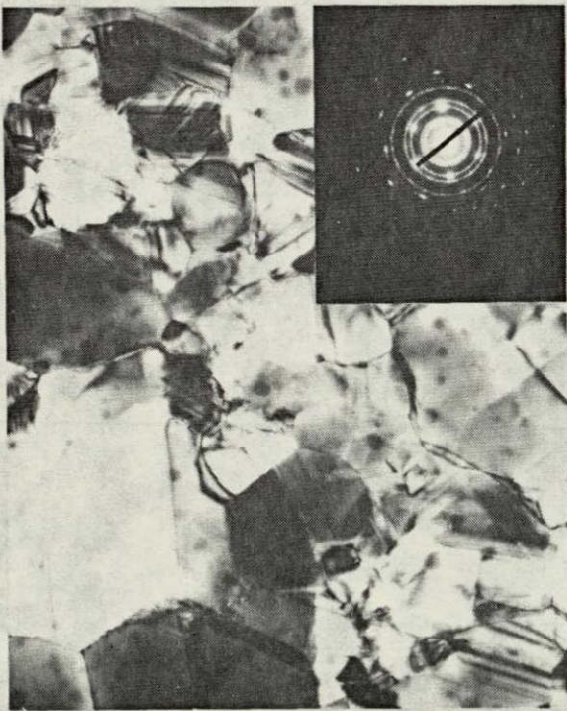


a

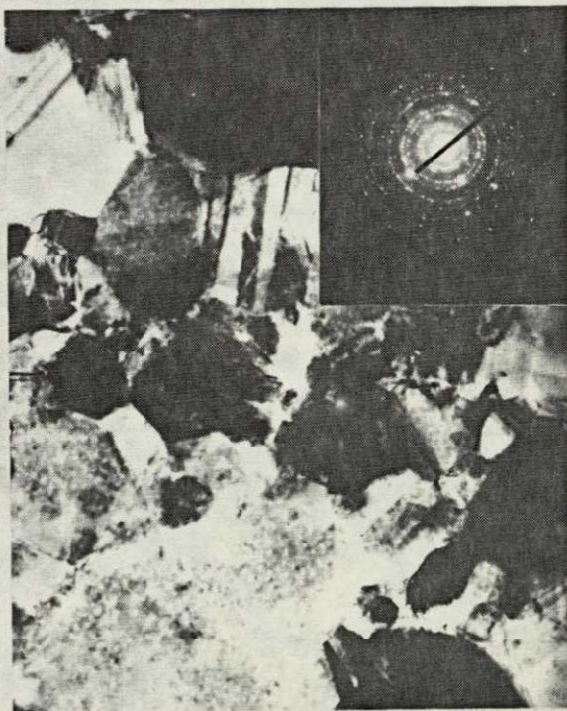


c

1700 Å



b



d

TABLE III
GRAIN SIZES OF FILMS

Run	Film #	Thickness	Grain Size
<u>Z</u>			
Mica	1	295 $\overset{\circ}{\text{\AA}}$	357 $\overset{\circ}{\text{\AA}}$
	4	773 $\overset{\circ}{\text{\AA}}$	880 $\overset{\circ}{\text{\AA}}$
<u>Z</u>			
Glass	5	270 $\overset{\circ}{\text{\AA}}$	473 $\overset{\circ}{\text{\AA}}$
	8	790 $\overset{\circ}{\text{\AA}}$	494 $\overset{\circ}{\text{\AA}}$
<u>F₁</u>			
Mica	1	200 $\overset{\circ}{\text{\AA}}$	305 $\overset{\circ}{\text{\AA}}$
	4	480 $\overset{\circ}{\text{\AA}}$	357 $\overset{\circ}{\text{\AA}}$
	12	975 $\overset{\circ}{\text{\AA}}$	678 $\overset{\circ}{\text{\AA}}$
<u>F₁</u>			
Glass	5	200 $\overset{\circ}{\text{\AA}}$	236 $\overset{\circ}{\text{\AA}}$
	7	400 $\overset{\circ}{\text{\AA}}$	446 $\overset{\circ}{\text{\AA}}$
	10	650 $\overset{\circ}{\text{\AA}}$	497 $\overset{\circ}{\text{\AA}}$
<u>G₁</u>			
Mica	3	423 $\overset{\circ}{\text{\AA}}$	883 $\overset{\circ}{\text{\AA}}$
	4	761 $\overset{\circ}{\text{\AA}}$	971 $\overset{\circ}{\text{\AA}}$
<u>G₁</u>			
Glass	6	295 $\overset{\circ}{\text{\AA}}$	572 $\overset{\circ}{\text{\AA}}$
	8	753 $\overset{\circ}{\text{\AA}}$	911 $\overset{\circ}{\text{\AA}}$

DATA ANALYSIS

For polycrystalline films where the grain size approaches or is less than that of the thicknesses, grain boundary scattering can become a significant factor in film resistivity. Mayadas and Shatzkes¹³ (M-S) theory for incorporating grain boundary scattering is used for the data analysis along with the linear approximation to the M-S theory by Mola and Heras.¹⁴

The M-S theory is based on the assumption that there is an average grain diameter, D . The M-S theory is expressed by

$$\rho_f/\rho_g = [1-A/f(\alpha)]^{-1} \quad (1)$$

where

$$A = \frac{6}{K_0 \pi} (1-P) \int_0^{\pi/2} d\phi \int_1^{\infty} dt \frac{\cos^2 \phi}{H^2(t, \phi)} \left(\frac{1}{t^3} - \frac{1}{t^5} \right) \frac{(1 - e^{-K_0 t H(t, \phi)})}{(1 - P e^{-K_0 t H(t, \phi)})} \quad (2)$$

$$f(\alpha) = 1 - \left(\frac{3}{2}\right)\alpha + 3\alpha^2 - 3\alpha^3 \ln(1 - 1/\alpha) = \rho_o/\rho_g \quad (3)$$

$$\alpha/l_o = \frac{1}{D} \frac{R}{1-R} \quad (4)$$

¹³A. F. Mayadas and M. Shatzkes, op. cit.

¹⁴E. Mola and J. Heras, "Numerical Evaluation of the Resistivity of Poly-Crystalline Metal Films with the Mayadas-Shatzkes Model," Electrocomponent Science and Technology, 1 (September, 1974), pp. 77-78.

$$H(t, \phi) = 1 + \alpha / \cos \phi (1 - \frac{1}{t^2})^{1/2}$$

ρ_f = Film resistivity

ρ_g = Resistivity from grain boundary scattering

ρ_o = Film resistivity without size effects

a = Film thickness

l_o = Mean free path of electron

D = Grain size

R = % of electrons scattered at grain boundary

P = Specularity parameter

$K_o = a/l_o$

The value of R can vary from 0 for no reflection of the electrons from the grain boundaries to 1 for every electron reflected and P varies from 0 for diffuse scattering from the surfaces to 1 for completely specular scattering.

One of the linearized approximations of M-S due to Mola and Heras which assumes $D = a$ is:

$$\rho_f / \rho_o = 1 + M(P, R) l_o / a \quad (5)$$

A functional form for $M(P, R)$ was fitted to Mola and Heras' results by Longbrake.¹⁵

$$M(P, R) = [1.3049 R / 1 - R + .457(1 - P)] \quad (6)$$

¹⁵ Ibid.

Therefore from a linear least squares fit of ρ_f vs. $1/a$ the slope is used to obtain the value of R over a range of P when the value of the product is known. The intercept yields ρ_o . If the assumption $D = a$ is replaced by $D = Ca$ then resistivity data where grain diameter is not equal to film thickness may be analyzed if the constant C can be determined.

An approximate form of M-S theory which makes use of the $M(P,R)$ functional form is given by:¹⁶

$$a = \rho_g / R_{sq} + 6(1-P)(l_o / [\pi f(\alpha)]) \iint \quad (7)$$

where

$$R_{sq} = \rho/a \text{ and } \iint \text{ is the double integral in eq. (2)}$$

In rewriting the expression the largest error, thickness measurement, is approximately removed from the independent variable. A weighted least squares analysis of a vs. $1/R_{sq}$ yields the value of ρ_g if the $\iint$ is assumed to be a slowly varying function of K_o and is calculated using an average value of K_o for a given temperature. From the intercept value an iterative calculation yields the value of P . The bulk values of resistivities for the material, ρ_o , are obtained from the published data of Meaden.¹⁷ Utilizing the

¹⁶J. Brient, Private communication.

¹⁷George Terence Meaden, Electrical Resistance of Metals (New York: Plenum Press, 1965), pp. 15-16.

ratio ρ_o/ρ_g and equation (3) the value of α was obtained. The value of α/l_o was calculated for the gold and silver film using the values of l_o determined from the values of ρ_o and the product $\rho_o l_o$ from Hubin and Gouault.¹⁸ Values for R were determined, once the average grain size D was available, from equation (4).

Results

Examination of the micrographs reveals that for some of the films the grain size is relatively constant with thickness and for others the grain size is proportional to film thickness. Thus a separate analysis was used for each of these groups.

Run Z. Since the final data cycle for this run included an additional evaporation of $150\text{\AA}$ and annealed to a much higher temperature (450K) than the previous data cycles (350K), the micrographs for this run correspond to the higher annealing temperature as well as a multiple layer film.

From the analysis of the films on mica the micrographs showed a grain size dependence on thickness for the two thicknesses examined. Assuming a linear relation between D and a, measurements on the micrographs yield the value of the constant in the expression $D = Ca$ and the linearized form of M-S theory (equation 5) is used to analyze the data.

¹⁸M. Hubin and J. Gouault, "Resistivity and Thermo-electric Power Between -100°C and $+100^\circ\text{C}$ of Gold and Silver Thin Films Formed and Studied in Ultrahigh Vacuum," Thin Solid Films, 24 (1974), pp. 311-331.

From Table IVa the values for R are shown under the linearized M-S theory. This analysis indicates the reflection of electrons at the boundaries is close to 100% (i.e. $R = 1$). The analysis is independent of the value of P any value of P from 0 to 1 yielding the same value of R. The data was also analyzed by using the approximate theory of M-S (equation 7) where an average of the two grain sizes was used for the value of D. In this analysis the R values are of the order of 60%.

For the films deposited on glass the grain size is relatively constant. The approximate M-S theory (equation 7) is used to analyze the data. An average grain size of $484\text{\AA}$ was used in calculating the reflection coefficients. Table IVa lists the values of R and P for the range of temperatures measured. The reflection coefficient is 60 to 70%, of the same order as that of the mica films analyzed in the same fashion. In addition the surface scattering is specular, $P = 1$.

For the initial data cycles there are no corresponding micrographs. The M-S analysis for the approximate form is applied to this data (equation 7). Results show that the values of $\alpha/l_0 [=1/D R/1-R]$ are of the same order although smaller than those for the films on glass and mica for the final annealed data. R values using the same $484\text{\AA}$ average grain diameters are indicated. It should be noted that although micrographs are not available for the initial deposition or for the thin overlayer deposition the structure

TABLE IVa

DATA ANALYSIS OF RUN Z - Au

APPROXIMATE M-S ANALYSIS

Substrate	Temperature (Deg. K)	$\alpha/l_o (\times 10^{-3} \text{\AA}^{-1})$	P	R
Initial Deposition of Films				
Mica:	170 ^o $\text{\AA}$, 245 ^o $\text{\AA}$, 398 ^o $\text{\AA}$, 550 ^o $\text{\AA}$, 734 ^o $\text{\AA}$, 854 ^o $\text{\AA}$			
Glass:	145 ^o $\text{\AA}$, 270 ^o $\text{\AA}$, 415 ^o $\text{\AA}$, 567 ^o $\text{\AA}$, 735 ^o $\text{\AA}$			
Mica	144	2.26	1	.58
	295	2.38	0	.60
	337	3.37	0	.68
Glass	144	2.56	1	.55
	295	2.76	0	.57
	337	2.80	0	.58
Deposition of 10-50 ^o $\text{\AA}$ Onto All Films				
Mica:	195 ^o $\text{\AA}$, 270 ^o $\text{\AA}$, 423 ^o $\text{\AA}$, 575 ^o $\text{\AA}$, 759 ^o $\text{\AA}$, 876 ^o $\text{\AA}$			
Glass:	170 $\text{\AA}$, 295 $\text{\AA}$, 440 $\text{\AA}$, 592 $\text{\AA}$, 760 $\text{\AA}$			
Mica	140	2.23	1	.58
	295	2.35	0	.59
Glass	140	2.53	1	.55
	295	2.83	0	.58

TABLE IVa (continued)

Substrate	Temperature (Deg. K)	$\alpha/l_0 (\times 10^{-3} \text{ } ^\circ\text{A}^{-1})$	P	R
Deposition of $\approx 150 \text{ } ^\circ\text{A}$ Onto All Films				
Mica: $295 \text{ } ^\circ\text{A}$, $490 \text{ } ^\circ\text{A}$, $630 \text{ } ^\circ\text{A}$, $773 \text{ } ^\circ\text{A}$, $893 \text{ } ^\circ\text{A}$, $1135 \text{ } ^\circ\text{A}$				
Mica D = $619 \text{ } ^\circ\text{A}$				
Glass: $270 \text{ } ^\circ\text{A}$, $505 \text{ } ^\circ\text{A}$, $647 \text{ } ^\circ\text{A}$, $790 \text{ } ^\circ\text{A}$, $894 \text{ } ^\circ\text{A}$				
Glass D = $484 \text{ } ^\circ\text{A}$				
Mica	151	2.58	1	.62
	294	2.78	1	.63
	455	2.79	0	.63
Glass	151	2.66	1	.56
	294	3.37	1	.62
	455	3.45	1	.63
Linearized M-S Theory				
This analysis is for mica films after deposition of $\approx 150 \text{ } ^\circ\text{A}$.				
Mica: $295 \text{ } ^\circ\text{A}$, $490 \text{ } ^\circ\text{A}$, $630 \text{ } ^\circ\text{A}$, $773 \text{ } ^\circ\text{A}$, $893 \text{ } ^\circ\text{A}$, $1135 \text{ } ^\circ\text{A}$				
C = 1.09				
Temperature (Deg. K)	$M\rho_0 l_0$ ($\mu\Omega\text{-M-}^\circ\text{A}$)	ρ_0 ($\mu\Omega\text{-M}$)	P	R
151	1116	3.4	1-0	.98
294	1100	5.0	1-0	.98
455	760	6.8	1-0	.98

factor α/l_0 does not change significantly from that for the final films.

Run F₁. The analysis of gold films on mica using the linearized approximation to the M-S theory and $D = Ca$ is indicated in Table IVb. The first annealed data cycle shows a reflection of approximately 90%. The reflection coefficient was not sensitive to the values of the specularity parameter. After the addition of the 10-50^oA deposit to all the films the reflection coefficients' range was about 86% irregardless of the value of P.

The approximate M-S theory was also performed on these same mica films. The value of D used was an average of the grain size of the three films examined. The values for the reflection coefficients were approximately 35% for both annealed data runs.

Those gold films deposited on glass were only analyzed by utilizing the approximate form of the M-S theory expressed in equation (7). Significantly lower values of R were obtained for the films on glass ($\approx 29\%$ compared with $\approx 36\%$ on mica). Also the values of P indicate completely diffuse scattering from films on glass substrates compared with specular scattering from films on mica substrates.

Run G₁. Although these silver films, both those evaporated on glass and those on mica, appeared to have grain size that were not constant with thickness the linearized M-S analysis resulted in ρ_0 less than the Meaden values. When

TABLE IVb

DATA ANALYSIS OF RUN F₁ - Au
APPROXIMATE M-S ANALYSIS

Substrate	Temperature (Deg. K)	$\alpha/l_o (x10^{-3})$	P	R
Initial Deposition of Films				
Grain size used in analysis: Mica, 446 $\overset{\circ}{\text{\AA}}$. Glass, 437 $\overset{\circ}{\text{\AA}}$.				
Mica: 330 $\overset{\circ}{\text{\AA}}$, 340 $\overset{\circ}{\text{\AA}}$, 650 $\overset{\circ}{\text{\AA}}$, 975 $\overset{\circ}{\text{\AA}}$				
Glass: 270 $\overset{\circ}{\text{\AA}}$, 400 $\overset{\circ}{\text{\AA}}$, 650 $\overset{\circ}{\text{\AA}}$, 950 $\overset{\circ}{\text{\AA}}$				
Mica	117	1.14	1	.34
	293	1.26	1	.36
	446	1.37	1	.38
Glass	117	.874	—0	.28
	293	.968	0	.30
	446	.970	0	.30
Deposition of 10-50 $\overset{\circ}{\text{\AA}}$ Onto All Films				
Mica	117	1.13	1	.34
	292	1.26	1	.36
	446	1.39	.7	.38
Glass	117	.850	.1	.27
	292	.930	0	.29
	446	.920	0	.29

TABLE IVb (continued)

Linearized M-S Theory				
This analysis applied only to mica films.				
Mica: 330 $\overset{\circ}{\text{\AA}}$, 340 $\overset{\circ}{\text{\AA}}$, 650 $\overset{\circ}{\text{\AA}}$				
C = .65				
Temperature (Deg. K)	$M\rho_0 l_0$ ($\mu\Omega\text{-M-}\overset{\circ}{\text{\AA}}$)	ρ_0 ($\mu\Omega\text{-M}$)	P	R
117	443	1.27	1-0	.89
293	506	2.63	1-0	.90
446	614	3.69	1-0	.92
Deposition of 10-50 $\overset{\circ}{\text{\AA}}$ Onto All Films				
117	322	1.39	1-0	.85
292	342	2.76	1-0	.86
446	391	3.84	1-0	.87

the approximate M-S analysis of equation (7) was applied to these films, both the films on glass and mica resulted in reflections in the order of 10 to 20% and large P values indicating specular services as shown in Table IVc.

Run H₁. Since the thicknesses of these films were so large in comparison with the three previous runs micrographs of these could not be obtained. The approximate form of M-S analysis, equation (7), is indicated in Table IVd.

For the mica in the first annealed data run the range of α/l_0 ($\times 10^{-3}$) is from .53 to 2.2 while for the glass the values are .88 to 5.1. After a $\approx 150\text{\AA}$ film is deposited on all the films and annealed the values of α/l_0 ($\times 10^{-3}$) for mica are .58 to 2.5 and .94 to 5.4 for glass. The variation of α/l_0 , the structure factor, with temperature indicates the weak dependence of this data on size effect as previously noted when discussing the data for this run in Figure 10.

TABLE IVc

DATA ANALYSIS OF RUN G₁ - Ag

APPROXIMATE M-S ANALYSIS

Substrate	Temperature (Deg. K)	$\alpha/l_0 (\times 10^{-3} \text{\AA}^{-1})$	P	R
Initial Deposition of Films				
Grain size used in analysis: Mica, 827 $\text{\AA}$. Glass, 742 $\text{\AA}$.				
Mica: 316 $\text{\AA}$, 423 $\text{\AA}$, 761 $\text{\AA}$, 714 $\text{\AA}$, 982 $\text{\AA}$				
Glass: 461 $\text{\AA}$, 753 $\text{\AA}$, 910 $\text{\AA}$				
Mica	105	.245	.84	.17
	292	.306	.74	.20
	456	.345	.65	.22
Glass	105	.150	.68	.10
	292	.290	.94	.18
	456	.434	.73	.24
Deposition of 10-50 $\text{\AA}$ Onto All Films				
Mica	105	.236	.83	.16
	295	.287	.84	.19
	397	.319	.67	.21
Glass	105	.137	.67	.09
	295	.237	.97	.15
	397	.380	.70	.22

TABLE IVd
DATA ANALYSIS OF RUN H₁ - Pb
APPROXIMATE M-S ANALYSIS

Substrate	Temperature (Deg. K)	α/l_0 ($\times 10^{-3} \text{\AA}^{-1}$)	P
Initial Deposition of Films			
Mica:	2086 $\text{\AA}$, 3429 $\text{\AA}$, 5276 $\text{\AA}$, 6379 $\text{\AA}$, 7481 $\text{\AA}$		
Glass:	4269 $\text{\AA}$, 6510 $\text{\AA}$, 9030 $\text{\AA}$		
Mica	103	.534	1
	298	.922	1
	430	2.24	1
Glass	103	.881	1
	298	3.13	1
	430	5.09	1
Deposition of $\approx 150 \text{\AA}$ Onto All Films			
Mica	102	.576	1
	295	.916	1
	451	2.53	1
Glass	102	.94	1
	295	3.03	1
	451	5.38	1

DISCUSSION

The analysis of size effect of the films using M-S Theory is very sensitive to the values of a . A 5% variation of a , well within the error of thickness measurements, is the difference between analyzable data and that which is not analyzable. This emphasizes the need for accurate and high resolution thickness measurements. There is also a question about whether the thermocouples are measuring the changing temperature of the films when they are located on the front face of a substrate on the substrate holder. This can be resolved if thin film thermocouples are deposited adjacent to the films and used to monitor the temperature.

APPENDIX

.

QUARTZ CRYSTAL CALIBRATION

During the film deposition the thickness growth of the films is monitored through a quartz crystal oscillator. The thickness is determined from the frequency of the quartz crystal by using the relation $T = 2F/D$, where T is the thickness, F is the frequency change, and D is the density of the metal. Calibration is achieved by determining an equivalent density.

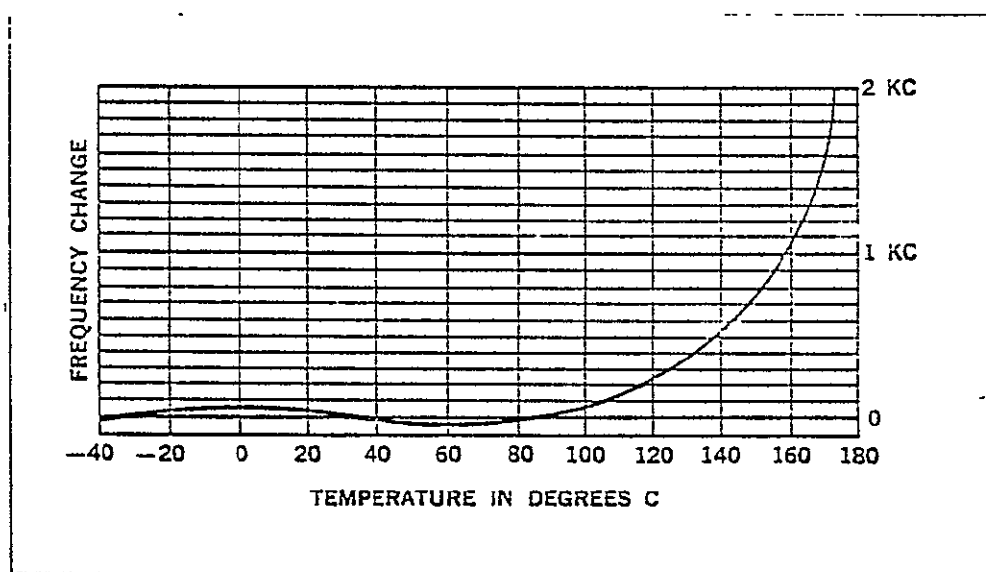
Initially the bulk density is used in the evaporation. Once the data runs have been completed and film thicknesses are measured the oscillator is calibrated. From the above relation it can be seen that a plot of $2F$ vs. T gives the density of the metal.

Of course this calibration only holds when the same geometry is repeated and the same deposition parameters are used. In order for this calibration to hold true in addition to maintaining the same system configuration the quartz crystal oscillator must be maintained at the same temperature throughout the evaporation. The reason for this added control is that the quartz crystal frequency is very sensitive to temperatures. Figure 14 is a graph of the frequency response with temperature.¹⁹ From the figure the most desirable range to be in is that from 20°C to 80°C since a

¹⁹Sloan Technology Corporation, "Sloan OMNI IIA Deposition Control Master Manual," p. 4-3.

Figure 14. Temperature Coefficient of Oscillation of Quartz Crystals.

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temperature change in this range results in a less than 10% frequency change.

In order to monitor this temperature change a thermocouple was attached to the oscillator housing. It was placed in such a way as to be in contact with the quartz crystal but not interfere with its oscillations. A reservoir capable of heating water was attached to the copper tube that is attached to the housing. This copper tube is used as a conduction cooling line. By controlling the temperature of the water through it the temperature of the oscillator can be maintained within a desired range. Since the stainless steel housing is relatively massive the temperature effect of the heated water reservoir was not as large as anticipated. Another crystal oscillator holder was obtained which has only the housing for the crystal inside the vacuum chamber. This crystal holder being much less massive will be more susceptible to temperature control. Table V contains calculated values for the effective density for several runs.

TABLE V

QUARTZ CRYSTAL OSCILLATOR CALIBRATION

Run	Rate	Substrate Temperature	Density (gm/cm ³)	Calibrated Density	Range of Thickness	Temperature Change of Oscillator
Z-Au	10 ⁰ Å/s	340K	19.3	18.7	300- 1,100 ⁰ Å	320-322K
F ₁ -Au	5 ⁰ Å/s	380K 450K	19.3	18.75	200- 1,000 ⁰ Å	401-403K
G ₁ -Ag	14 ⁰ Å/s	450K	10.5	10.96	300- 1,000 ⁰ Å	399-400K
H ₁ -Pb	28 ⁰ Å/s	450K	11.3	11.0*	4,000-15,000 ⁰ Å	392-395K

*Only thicknesses of films on glass used.

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